



LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

Equation of State Measurements by Radiography Provide Evidence for a Liquid-Liquid Phase Transition in Cerium

M. J. Lipp, Z. Jenei, D. Ruddle, C. Aracne-Ruddle, H. Cynn, W. J. Evans, Y. Kono, C. Kenney-Benson, C. Park

September 8, 2013

Journal of Physics: Conference Series

Disclaimer

This document was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor Lawrence Livermore National Security, LLC, nor any of their employees makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or Lawrence Livermore National Security, LLC. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or Lawrence Livermore National Security, LLC, and shall not be used for advertising or product endorsement purposes.

Equation of state measurements by radiography provide evidence for a liquid-liquid phase transition in cerium

M. J. Lipp¹, Zs. Jenei¹, D. Ruddle¹, C. Aracne-Ruddle¹, H. Cynn¹, W.J. Evans¹, Y. Kono², C. Kenney-Benson², C. Park²

1) High Pressure Physics Group, Lawrence Livermore National Laboratory, Livermore, CA 94550

2) HPCAT, Geophysical Laboratory, Carnegie Institute of Washington, Argonne, IL 60439, USA

Abstract

A pressure-volume isotherm in cerium metal at 1100 K was measured in a large volume press of the Paris-Edinburgh type up to 6 GPa. The volume was determined by imaging a rectangular shape of the sample via white X-ray radiography. Energy dispersive x-ray diffraction spectra were recorded to ensure that the highly reactive cerium in the cell assembly remained pure at this temperature. Even at 1100 K the p-V equation of state of liquid cerium shows a pronounced decrease of the bulk modulus above the γ -phase region similar to the 775 K isotherm in the solid that also shows an inflection point between γ - and α -type cerium. The inflection point in the 1100 K isotherm indicating the minimum in the bulk modulus separating the γ - from the α -type liquid is located at approximately 3.5 GPa.

PACS numbers: 64.30.Ef , 64.70.Ja , 61.20.-p , 71.20.Eh

1. Introduction

Cerium's phase diagram exhibits a melt-line with a broad minimum [1] at ~ 3.3 GPa that was measured a long time ago in a large volume press of the piston cylinder type [1]. The melting temperature decreases linearly from 1070 K at ambient pressure to 935 K at the minimum (3.3 GPa) and then increases again sub-linearly. Pulsed laser heating experiments have extended the pressure range up to 30 GPa at which point the melting temperature has risen back up to 1370 K [2]. This peculiar behavior of the melt-line suggests that the liquid on the lower pressure side of the melt-line minimum has a density larger than the solid and the liquid on the high pressure side has a density lower than the solid (the "normal" case).

This could also mean that the liquid consists of two different kinds with a liquid-liquid transition between them. It is tempting to connect the two types of liquids with the two fcc phases of cerium at room temperature, the high volume (low pressure) γ -phase and the low volume (high pressure) α -phase which differ by ~ 15 % when crossing the volume collapse transition at 0.75 GPa. The nature of this iso-structural volume collapse has interested researchers since its discovery in 1927 [3] and has been the subject of numerous experimental and theoretical studies to this day [4-12]. This volume collapse transition is also observed for higher temperature isotherms but with decreasing volume change until the isotherm exhibits a horizontal dp/dV slope at 1.5 GPa and ~ 207 Celsius, defining the critical point with a zero bulk modulus [6]. Above the critical temperature the bulk modulus still displays a minimum (dip) versus pressure, the depth of which, however, decreases with increasing temperature, while the width increases [6] (see Figure 1). Presumably at even higher temperatures this dip will broaden out completely and this distinction between γ -like and α -like types will vanish [12].

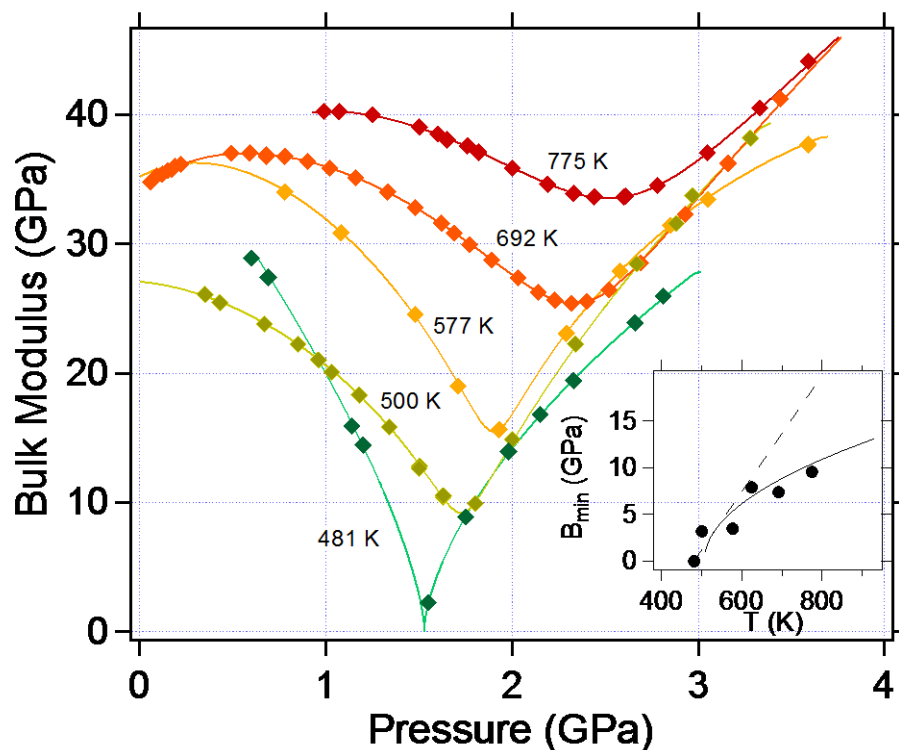


Figure 1. Selected isothermal bulk moduli of cerium at or above the critical point at 1.5 GPa and 481 K. For visual clarity the 500 K curve has been offset in the bulk modulus value by + 6 GPa, the 577 K one by 12 GPa, the 692 K one by 18 and the 775 K one by 24 GPa. The inset shows the value of the bulk modulus minimum (“dip”) and the dashed line the expected value based on the pseudo-binary liquid model [13].

Taking the second derivative of the bulk modulus versus pressure as a measure of the strength of the transition from γ -type to α -type one can establish that this strength decreases closer to the liquid (see Figure 2). The goal of this experiment was to see whether the transition continues on into the liquid regime and whether two different types of liquid can be identified as γ - and α -like extensions of their solid counter-parts.

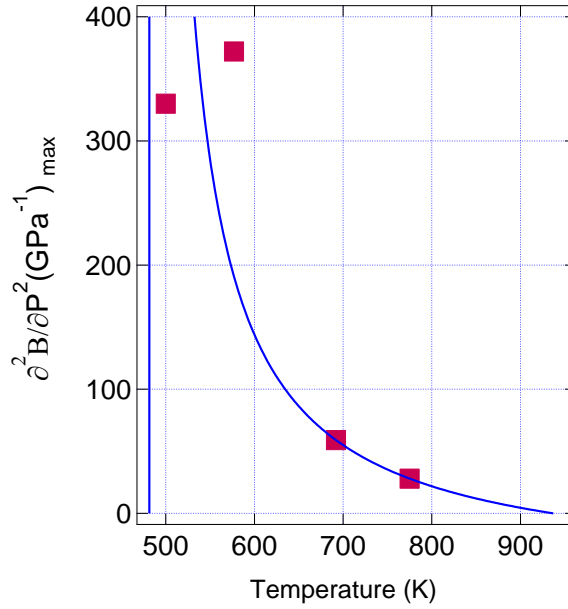


Figure 2. Maximum of the second derivative of the isothermal bulk modulus versus temperature. At the critical point (~ 481 K) the maximum is located at infinity. With higher temperature the maximum decreases. A hyperbolic fit to the data would indicate that the effect could vanish at ~ 940 K, very close to the minimum of the melting temperature at 3.3 GPa.

Measurements of the EOS of cerium at high temperature are difficult, especially in the liquid phase. We attempted numerous times to obtain data from cerium in the liquid in diamond anvil cells by resistive heating. However, cerium's reactivity in the melt as well as the long times required to record structure factor measurements (energy dispersive method [14]) resulted in cerium leaching out the carbon from the exposed surface of the diamond anvils and presumably forming cerium carbide. Structure factor studies also proved exceedingly difficult with energy dispersive methods in a large volume press since the time required for a sequence of measurements again allowed the liquid cerium to interact chemically with other constituents of the sample environment. Finally we settled on experiments using a large volume press with macroscopic samples that allowed us to observe the sample *in situ* while being heated quickly into the liquid (1100 K) at high pressure starting from a “safe” base temperature (775 K). The goal was to let the temperature stabilize over approximately two minutes, then image the sample via radiography and quickly return to the base temperature. A subsequent energy dispersive X-ray diffraction (EDX) pattern at the edge of the sample allowed us to assess whether the sample had started to react. The image was evaluated to measure the sample volume resulting in an equation of state in the liquid and an EDX pattern of the MgO provided the pressure value (using the EOS by [15]).

Obtaining an EOS by means other than X-ray diffraction has a long tradition. In the past, before the advent of the versatile diamond anvil cell, EOS measurements at various temperatures were undertaken in large volume presses, as demonstrated in the case of cerium [16]. A comparison of isotherms published back in 1960 with modern EOS obtained by angle dispersive X-ray diffraction (ADX) [6] is shown in Figure 3 below. Previously we have also used the X-ray shadow imaging technique (radiography) to find the EOS of amorphous substances in diamond anvil cells [17] and a

microscope based version in the visible part of the spectrum for determining the EOS of polymers [18]. EOS obtained carefully by these methods can compare well with those obtained by ADX or EDX.

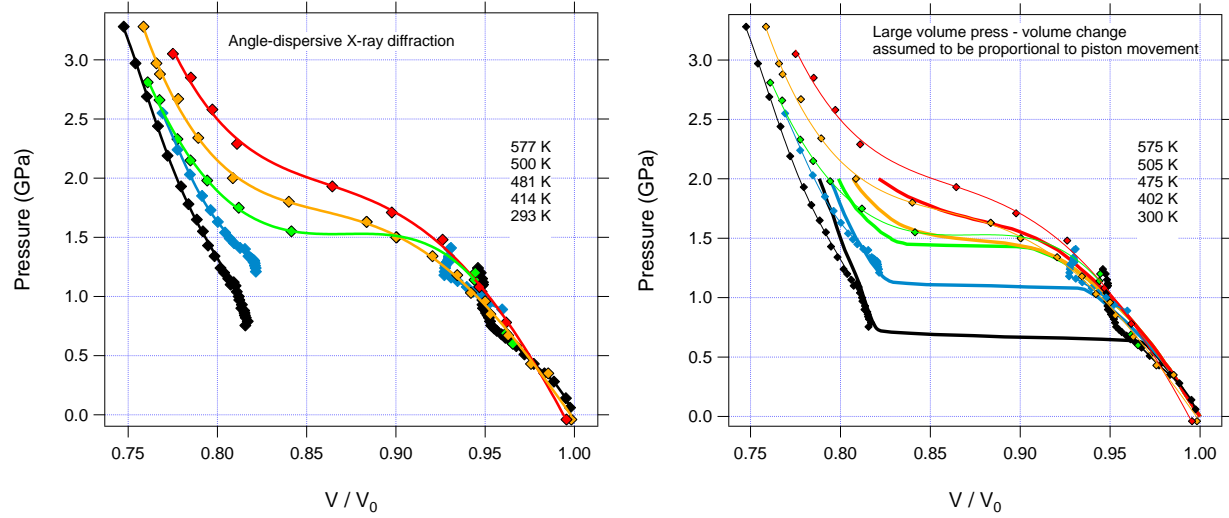
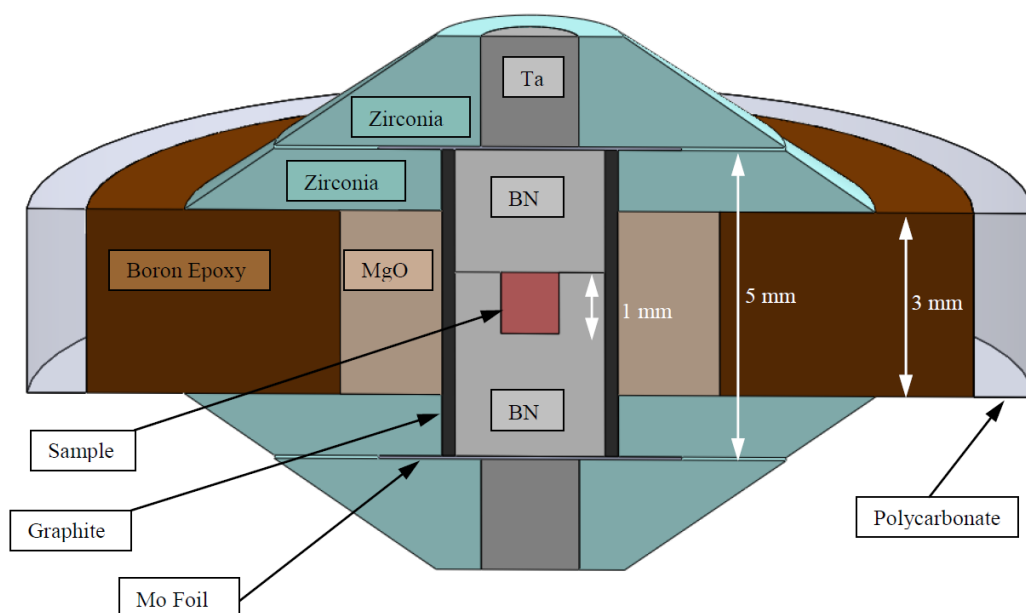


Figure 3. Comparison of cerium isothermal volume compression determined using a diamond anvil cell by ADX (left panel) with data obtained from a large volume press in 1960 (right panel) – the volume was assumed to be proportional to the sample thickness between the anvils as measured by a pointer attached to the movable piston– with modern EOS isotherms taken by ADX-diffraction drawn as thin lines in the right panel. At higher temperatures and pressures the large volume press data disagree severely with the inherently more accurate ADX data.

Our goal was to use simple sample shapes whose dimensions could be obtained by imaging to extract the volume information. Cerium appears to remain in its original shape in this sample environment even in the melt.

2. Experimental Details

The samples were commercially obtained from AlfaAesar in form of 0.5 to 1 mm thick foils with 99.9 % purity. Pucks were cored out into rectangular and round shapes to a diameter or side-length of $\sim 300 \mu\text{m}$ and polished down to a thickness of $\sim 250 \mu\text{m}$. Subsequent efforts showed that the rectangular samples delivered a better edge contrast when oriented square to the microscope and the following results refer to rectangular samples only. The samples were mounted in cylinders of crushable BN and loaded into the graphite heating cylinder which in turn was surrounded by a tube of MgO which also served as pressure marker. The temperature had been previously calibrated in reference to the dissipated power in the cell assembly [19]. Figure 4 shows the cell assembly as well as an image obtained by white beam radiography at zero pressure that even shows the dividing line between the individual BN pieces.



Top View of Completed Assembly

Side view of sample before compression

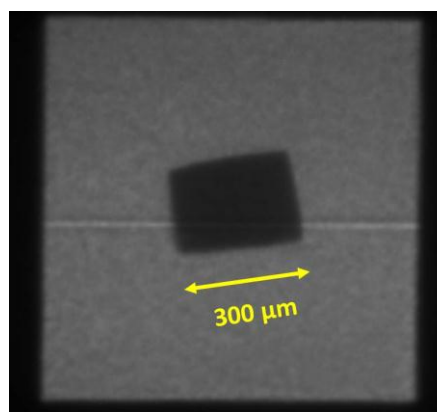
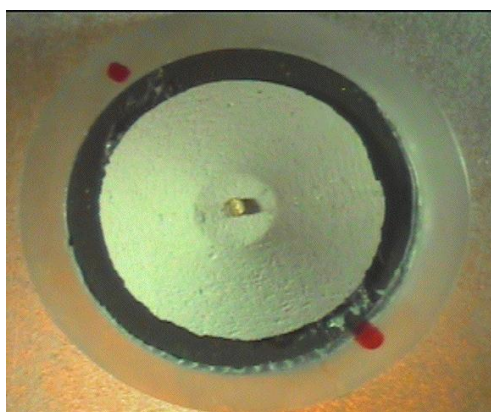


Figure 4. (top): Schematic of the cell assembly [20]; (bottom left): completed assembly before installation in the large volume press, a Paris Edinburg Cell at HPCAT; (bottom right): sample sitting inside cell assembly as imaged by white X-ray beam.

The experiment started by loading the sample in the proper orientation and compressing it at room temperature to ~ 5 GPa (while taking radiographic images) at which point heating commenced. The samples were heated to 500 Celsius (773 K) as base temperature. The radiographic images for the EOS at 1100 K and 775 K were taken while decompressing the sample assembly. If the assembly was first heated and then pressurized the lack of strength of the cell components led to too much deformation and prevented us from reaching high pressure. In order to prevent possible reactions with the surrounding BN

the heating to 1100 K was limited to about 2 – 3 minutes which was enough to have the temperature stabilize and then record an image. EDX was employed to monitor the sample for the formation of unwanted cerium compounds which, however, were not observed. The white X-ray beam created a shadow picture on a very thin (5 μm) Tb-doped gadolinium gallium garnet crystal scintillator which was imaged through a 20x Mitutoyo objective onto a fast video camera [20]. The optical image was calibrated to 0.946 micron / pixel although this had no bearing on the measurement of the EOS. Since the shape of the sample remained rectangular even in the liquid phase the dimensions of thickness and width were used to extract the volume at each pressure. The images taken at room temperature and 775 K were used to construct a radiographic EOS which was compared with the one determined by ADX and EDX [6, 21] and served as a validation of the method. In this way the 1100 K isothermal EOS was anchored to the ambient temperature and 775 K one. Data sets for which this anchoring did not succeed were discarded.

3. Results and Discussion

Figure 5 shows the 1100 K isotherm for cerium in the liquid state. Also shown are the other radiography data obtained at lower temperatures in the solid phase (squares) for comparison with the EOS obtained by ADX [6] and EDX [21] (filled and hollow diamonds).

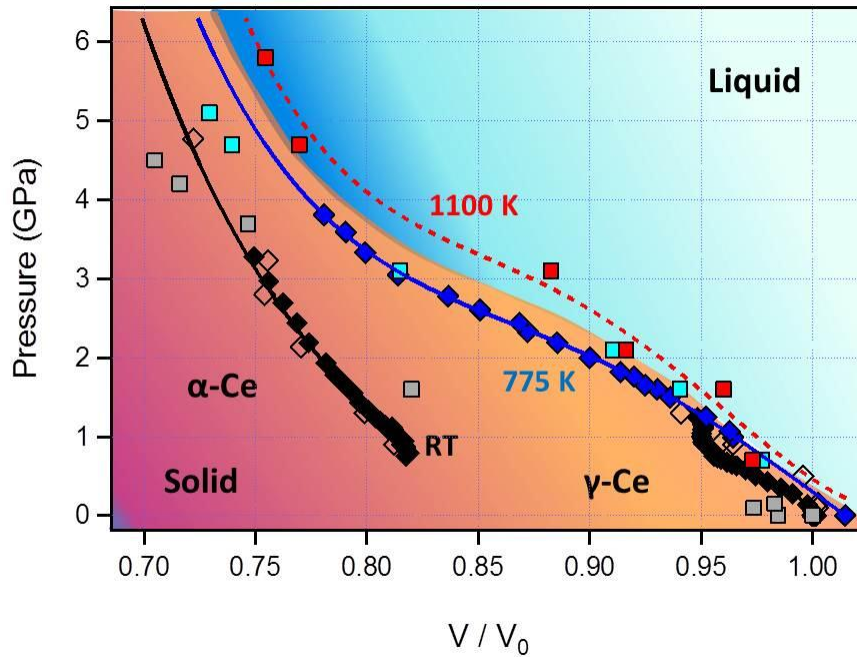


Figure 5. Isothermal volume compression data of cerium at high temperature and pressure. The equation of state of liquid cerium at 1100 K obtained by radiography is shown by red squares and a red dashed line. The solid-liquid boundary runs between the 775 K isotherm (blue) and the 1100 K isotherm. The data clearly show a γ -type liquid that runs very close to the other isotherms in the γ -phase and an α -type isotherm at higher pressures. The inflection point lies close to 3.5 GPa. Also shown are radiography results (squares) at RT (grey) and 775 K (light blue) together with data obtained by X-ray diffraction

(diamonds). Angle dispersive data are represented by filled diamonds [6], and energy dispersive by hollow diamonds [21].

Our radiography and the X-ray diffraction data are in relatively good agreement which lends further support to the quality of the data taken at 1100 K. The dashed red line connecting the data-points at 1100 K is a guide to the eye.

Figure 5 also shows that cerium expands little in the liquid with temperature at larger volumes ($V/V_0 > 0.9$) just as in the solid phase in contrast to the behavior at the lower volume part in the α -phase. Clearly, the softness of the γ -type phase extends into the melt. Even without further detailed analysis one can also immediately estimate that the point of inflection on the EOS is located at $\sim 3.5 \pm 0.5$ GPa. Figure 6 shows the location of this bulk modulus minimum in the liquid phase as well as the location of the other minima in the solid phase above the critical point as hollow diamonds.

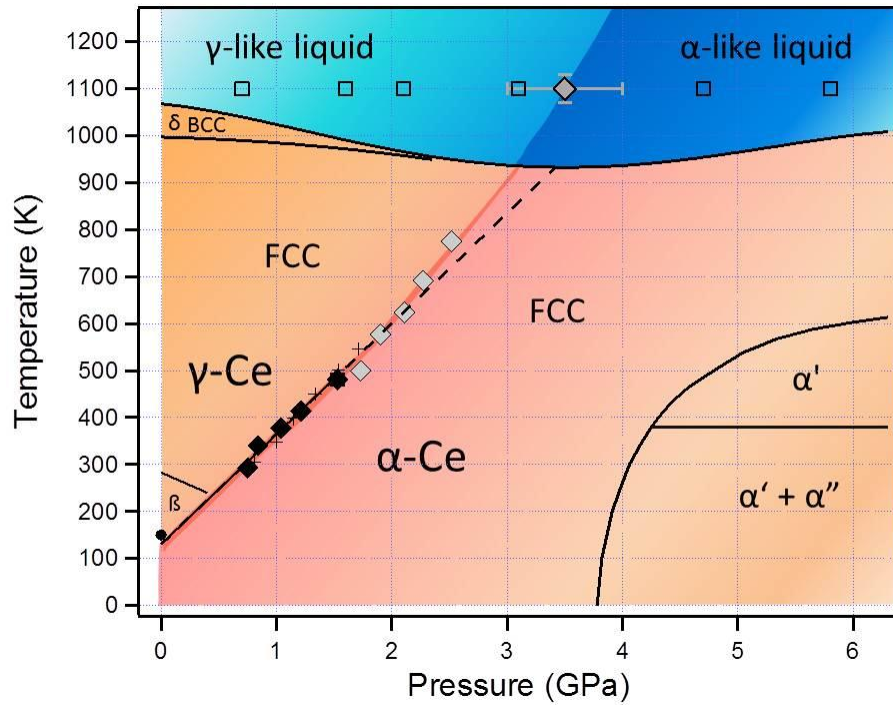


Figure 6. Phase diagram of cerium in the low pressure range showing the location of the bulk modulus minima above the critical point as grey filled diamonds in the solid and liquid phase. The hollow squares represent our radiography datapoints. Also indicated is the revised β - γ phase boundary [22].

The current quality of the data does not allow to say with certainty whether the minima veer slightly to the low pressure side of the melt-line minimum as shown in the figure or go straight through it as an extension of the dashed line which connects the locus of the first order volume collapse below the critical point with the minimum of the melt-line. Eliashberg and Capellmann expected the intersection to be at 2.5 GPa within a few kbar at most of the triple-point of liquid, γ - and δ -phase based on general thermodynamic arguments but they also assumed that the α -phase has a lower symmetry than the γ -phase [23]. In a purely pseudo-binary liquid model along the work of Aptekar' and Ponyatovskiy [13] one would expect the location of the bulk minima in figure 6 to follow the straight dashed line to the melt-line

minimum. The model also allows one to calculate the values of the bulk modulus at the dip, B_{\min} , which is shown in the inset to figure 1 as a straight dashed line versus temperature while the data start deviating from this line in a sub-linear fashion. The pseudo-binary liquid model explains the behavior qualitatively well, but it cannot account for these deviations.

Recently Cadien et al. [24] published structure factor measurements (taken by ADX) for cerium in the liquid phase. They were obtained by laser heating the samples in a diamond anvil cell and found evidence at 13 GPa for a 14% volume change between a low density (LDL) at 1500 K and a high density liquid (HDL) at 1900 K. Additionally, in their supplemental material they show a transition from LDL to HDL at $\sim 1260 \pm 70$ K going from 1.9 to 4.0 GPa. The observed volume change of 16 % between 1.9 GPa, 1200 K and 4 GPa, 1330 K compares favorably with the volume change observed by us between the same pressures at 1100 K. Their measurements were supported by calculations in the Mott transition framework identifying the LDL with the trivalent low density f_0 ($5s^25p^66s^25d^1 4f^0$, no f-electron) component and the HDL with the tetravalent high density f_1 ($5s^25p^66s^25d^1 4f^1$, one f-electron) component. Their calculations also pointed toward a critical point in the liquid at 2100 K and 21.3 GPa. However, recent measurements have shown that at least at room temperature the f-electron does only partially delocalize when going from the γ - to the α - phase [25,26]. It is therefore more likely that Cadien et al.'s identification of the two liquid components needs to be modified to some type of γ - (LDL) and α -type (HDL) liquid.

4. Conclusion

We have measured the equation of state (EOS) of cerium in the liquid phase at 1100 K via radiography. It behaves very similar to other EOS in the solid phase above the critical point showing a decreasing bulk modulus in the higher volume part leading to an inflection point in volume compression, resulting in a minimum in the bulk modulus. The similarity to the solid EOS above the critical point indicates the existence of two different kinds of liquid based on their response to compression: a γ - and a α -type with a liquid-liquid transition at ~ 3.5 GPa (1100 K). This observation is in good agreement with another recent experimental observation based on structure factor measurements in the liquid by Cadien et al. [24] who observe ~ 16 % volume change between 1.9 GPa (1200 K) and 4.0 GPa (1330 K).

Acknowledgments

This work was performed under the auspices of the US Department of Energy by Lawrence Livermore National Laboratory under Contract No. DE-AC52-07NA27344 and funded by the Laboratory Directed Research and Development Program at LLNL under project tracking code 12-LW-014. Portions of this work were performed at HPCAT (Sector 16), Advanced Photon Source (APS), Argonne National Laboratory. HPCAT operations are supported by DOE-NNSA under Award No. DE-NA0001974 and DOE-BES under Award No. DE-FG02-99ER45775, with partial instrumentation funding by NSF. APS is supported by DOE-BES, under Contract No. DE-AC02-06CH11357.

References

- [1] Jayaraman A 1965 *Phys. Rev.* **137** A179
- [2] Sitaud B, P  r   J and Th  venin Th 1994 *High Pressure Research* **12** 175

- [3] Bridgman P W 1927 *Proc. Am. Acad. Arts Sci.* **62** 207
- [4] Lawson A W and Tang T Y 1949 *Phys. Rev.* **76** 301
- [5] Koskenmaki D C and Gschneidner K A Jr 1978 *Handbook on the Physics and Chemistry of Rare Earths* (Amsterdam: North- Holland) chapter 4 (Cerium) p 337
- [6] Lipp M J, Jackson D, Cynn H, Aracne C, Evans W J and McMahan A K 2008 *Phys. Rev. Lett.* **101** 165703
- [7] Decremps F, Belhadi L, Farber D L, Moore K T, Occelli F, Gauthier M, Polian A, Antonangeli D, Aracne-Ruddle C M and Amadon B 2011 *Phys. Rev. Lett.* **106** 065701
- [8] Johansson B 1974 *Phil. Mag.* **30** 469
- [9] Allen J W and Martin R M 1982 *Phys. Rev. Lett.* **49** 1006
- [10] Lavagna M, Lacroix C and Cyrot M 1982 *Phys. Lett. A* **90**, 210
- [11] Allen J W and Liu L Z 1992 *Phys. Rev. B* **46** 5047
- [12] Wang Y, Hector L G Jr, Zhang H, Shang S L, Chen L Q and Liu Z K 2008 *Phys. Rev. B* **78**, 104113
- [13] Aptekar' I L and Ponyatovskiy Y G 1968 *Fiz. metal. metalloved.* **25** 777
- [14] Tsuji K, Yaoita K, Imai M, Shimomura O and Kikegawa T 1989 *Rev. Sci. Instr.* **60** 2425
- [15] Jackson I and Niesler H 1982 *High Pressure Research in Geophysics* (Tokyo: Center for Academic Publications) p 93
- [16] Beecroft R I and Swenson C A 1960 *J. Phys. Chem. Solids* **15** 234
- [17] Jenei Z, private communication
- [18] Lipp M J, private communication
- [19] Kono Y, Park C, Kenney Benson C, Shen G and Wang Y 201, submitted to *Physics of the Earth and Planetary Interiors* under review
- [20] Kono Y, Park C, Sakamaki T, Kenny-Benson C, Shen G and Wang Y 2012 *Rev. Sci. Instr.* **83** 033905
- [21] Olsen J S Gerward L Benedict U and Itié J-P 1985 *Physica* **133B** 129
- [22] Gschneidner K A, Pecharsky V K, Cho J and Martin S W 1996 *Scripta Materialia* **34** 1717
- [23] Eliashberg G and Capellmann H 1998 *JETP Letters* **67** 125
- [24] Cadien A, Hu Q Y, Meng Y, Cheng Y Q, Chen M W, Shu J F, Mao H K and Sheng H W 2013 *Phys. Rev. Lett.* **110** 125503
- [25] Rueff J-P, Itié J-P, Taguchi M, Hague C F, Mariot J-M, Delaunay R, Kappler J-P and Jaouen N 2006 *Phys. Rev. Lett.* **96** 237403
- [26] Lipp M J, Sorini A P, Bradley J, Maddox B, Moore K T, Cynn H, Devereaux T P, Xiao Y, Chow P and Evans W J 2012 *Phys. Rev. Lett.* **109** 195705